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EVALUATION OF OPERATING PARAMETERS OF ALUMINA COLUMNS FOR THE SELECTIVE REMOVAL OF PHOSPHORUS FROM WASTE-WATERS AND THE ULTIMATE DISPOSAL OF PHOSPHORUS AS CALCIUM PHOSPHATE

L. L. Ames

Battelle-Northwest
Richland, Washington

March 1969

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ROBERT A. TAFT WATER RESEARCH CENTER

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ALUMINA COLUMNS FOR SELECTIVE REMOVAL OF PHOSPHORUS FROM WASTEWATER

ADVANCED WASTE TREATMENT RESEARCH LABORATORY -VIII

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FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
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Cincinnati, Ohio

EVALUATION OF OPERATING PARAMETERS OF ALUMINA COLUMNS FOR THE SELECTIVE REMOVAL OF PHOSPHORUS FROM WASTEWATERS AND THE ULTIMATE DISPOSAL OF PHOSPHORUS AS CALCIUM PHOSPHATE

by

L. L. Ames

for

The Advanced Waste Treatment Research Laboratory
Robert A. Taft Water Research Center

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U. S. Department of the Interior
Federal Water Pollution Control Administration
Cincinnati, Ohio

March 1969

FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research studies carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

Reports in this series will be distributed as supplies permit. Requests should be sent to the Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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ABSTRACT

The use of high surface area alumina for phosphorus removal from wastewaters was investigated on a laboratory scale.

A synthetic secondary sewage effluent containing 10 to 30 mg PO_4/l, 300 mg HCO_3^-/l, 112 mg Cl^-/l and 50 mg SO_4^{-2}/l as anions and 130 mg Na^+/l, 60 mg Ca^{+2}/l, 25 mg each of K^+ and Mg^{+2} and 20 mg NH_4^+/l as cations was composited. With the above synthetic sewage effluent and 7.6 ml alumina columns, the effects of various compositional changes on phosphorus removal were ascertained.

The concentration of Mg^{+2} and Ca^{+2} showed marked effects on alumina column phosphorus capacity, with the phosphorus capacity about half for the solution containing no Ca^{+2} or Mg^{+2} as compared to solutions containing the above Ca^{+2} and Mg^{+2} concentrations. Probably adsorption onto the alumina occurs partly as a calcium or magnesium phosphorus complex rather than as a simple phosphorus anion. This notion is supported by the fact that reducing the phosphorus content of the influent solution by one-third only increases column capacity by a factor of two rather than three. Increasing the competing sulfate concentration in the influent solution to 4800 mg SO_4^{-2}/l showed little effect on phosphorus adsorption by alumina. Raising the pH of the synthetic sewage effluent to greater than 8.0 led to precipitation of calcium carbonate on the alumina grains which progressively lowered alumina phosphorus capacity. This problem was not encountered when using actual sewage effluent. It was found that alumina columns could be satisfactorily regenerated with NaOH. An acidic wash was not required.

Sewage effluent from the Richland trickling filter plant was used in scaleup to one liter alumina columns. Approximately 400 column volumes of Richland effluent were required for a 20 to 50 mesh, 275 m^2/g alumina column to reach 10% phosphorus breakthrough. If two columns were operated in series, more than 600 column volumes could be loaded on the first column before elution would be required.

Elution of phosphorus was accomplished with eight column volumes of 2M NaOH, followed by 20 column volumes of washwater. The column was then ready for reloading with phosphorus. If the column is drained at the end of the elution, NaOH losses are about 5% of a column volume per elution. The washwater containing phosphorus and NaOH washings can be recycled back to the sewage plant headend. The eight plus column volumes of NaOH contaminated with HCO_3^- and phosphorus, as well as organic coloring matter, can be cleaned by addition of 1.25 to 6.25 g/l of lime. The phosphorus is removed as $Ca_5(PO_4)OH$ (hydroxyapatite) and the HCO_3^- as $CaCO_3$ (Calcite). The coloring matter settles out with the above solids, allowing reuse of the NaOH. Thus only a small volume of solid waste is produced by the phosphorus removal process.

INTRODUCTION

Sawyer[12] has stated that phosphorus may represent the major uncontrolled pollutant now released to the environment in wastewater. According to Stephan[17], the average soluble phosphorus content of municipal secondary effluent is 25 mg PO_4/l, measured as orthophosphate. Other anions include Cl^- at 130 mg/l, NO_3^- at 15 mg/l, HCO_3^- at 300 mg/l, and SO_4^{-2} at 100 mg/l. Combined chemical-biological sewage treatment and phosphorus removal systems are now under study and development[1,3,5,18] as well as tertiary chemical-physical removal processes[2,4,9,16]. The above treatment systems, however, operate most economically as large-scale processes. A simple, economical phosphorus removal process would be desirable for the smaller, one to ten million gallons/day trickling filter sewage treatment plants. A phosphorus polishing process may also be required for the larger, combined treatment plants.

Few, if any, of the suggested or proven chemical-physical processes for phosphorus removal have contemplated the use of ion exchange. There is little economic incentive for employing an ion exchange process for phosphorus removal as Table 1 illustrates. Dowex 1 is a typical, strongly basic polystyrene matrix resin. The SO_4^{-2} constant was not given, but could be expected to be considerably higher than that of any of the above univalent anions. Use of an organic resin, then, requires removal of nearly all the other anions in addition to phosphorus, resulting in a liter of resin treating 40 liters or less, of average secondary sewage effluent containing approximately 600 mg/l of assorted anions.

Table 1

Anion exchange equilibrium constant (k) measurements on chloride Dowex 1 resin[11]

Anion	k	Anion	k
I^-	8.7	HCO_3^-	0.32
HSO_4^-	4.1	$H_2PO_4^-$	0.25
NO_3^-	3.8	OH^-	0.09
Cl^-	1.0		

In addition to low phosphorus removal efficiency, the problems of disposal of large regenerant waste volumes and use of relatively large process equipment are encountered with nonselective processes. Plainly, a more phosphorus-selective adsorbent is required if adsorption removal processes are to be economically attractive. Such a potentially economical process is available by utilizing alumina in adsorption columns.

Alumina ore, or bauxite, characteristically occurs in nature as an impure weathering product of aluminous rocks, and contains a mixture of gibbsite, boehmite and diaspore. According to the 1967 Minerals Yearbook, production of bauxite in 1966 was 40 million long tons with the United States consuming about one-third of world production. About six million tons of 99% purity alumina are produced annually in the United States, chiefly for use in the aluminum metal industry, but also for use in the abrasive, refractory and chemical industries.

As the composition of bauxite implies, several crystalline modifications of hydrated and nonhydrated aluminas exist. Nomenclature differences present some difficulties, however, so that only a few names will be given as an example in Table 2 along with physical properties. All of the aluminas in Table 2 show reproducible X-ray diffraction patterns. The

Table 2

Some alumina crystal modifications

Comparable Structure	Nomenclature	Formula	Density g/ml
Alpha Alumina Trihydrate	Gibbsite	$Al(OH)_3$	2.42
Beta Alumina Trihydrate	Bayerite	$Al(OH)_3$	2.53
Alpha Alumina Monohydrate	Boehmite	AlO(OH)	3.01
Beta Alumina Monohydrate	Diaspore	AlO(OH)	3.44
Alpha Alumina	Corundum	Al_2O_3	3.98

formulae are given in the form which emphasizes that these are hydroxide (OH^--containing) compounds and not hydrated (H_2O-containing) compounds. Anion exchange reactions on aluminas then become probable. Schwab[13] stated, for example, that the adsorption of ions, both cations and anions, on alumina takes place by displacement of ions of equal sign contained in the alumina surface. Shuvaeva and Gapon[15] also interpreted alumina chromatographic separations to mean that ion exchange is the primary mechanism involved in ion removal. They also showed that secondary adsorption occurs during removal of multivalent ions. Shibata[14] gives a cation adsorption series on alumina, in decreasing order of preference as Fe^{+3}, Hg^{+2}, Pb^{+2}, Cu^{+2}, Zn^{+2}, Ca^{+2}, Ni^{+2}, Fe^{+2} and Mn^{+2}, approximately the adsorption order for a normal hydrated ion series. Kubli[8] found the anion alumina adsorption series, in order of decreasing preference, to be OH^-, PO_4^{-3}, $C_2O_4^{-2}$, F^-, SO_3^{-2}, CrO_4^{-2}, NO_2^-, Cl^-, NO_3^-, MnO_4^- and SO_4^{-2}.

Yee[19] first made use of the chromatographic properties of high surface area alumina for the selective removal of phosphorus from wastewater. He reported that a downflow, 2 ml, alumina column could process about 1000 column volumes of a synthetic waste containing 25 mg PO_4/l as orthophosphates only to one percent breakthrough. Upflow tests were run on larger 200 ml columns using low-level radioactive process wastewater containing about 1 to 3 mg PO_4/l and suspended solids. Yee estimated that about 20,000 column volumes of the above waste could be processed to one percent phosphate breakthrough in the effluent. Higher waste throughputs were reported for forms of phosphorus other than orthophosphates. However, since biological treatment hydrolyzes 90% or more of the phosphorus, orthophosphates will predominate.

In Yee's work, the adsorbed phosphorus was stripped from the alumina column with 1 M NaOH and reacidified with 1 M HNO_3 for a total of from 12 to 16 column volumes of regenerant waste produced. Alumina losses during regeneration were given as from 5 to 35 percent, depending on the type of alumina used. No continuous cycling data was given for phosphorus removal on alumina columns. Yee estimated that phosphorus removal from wastewaters

on alumina columns would be $39.00/million gal in the case of a 14 mg PO_4/l influent to $64.00/million gal for a 23 mg PO_4/l influent. Eight percent/cycle alumina losses were assumed in the above cost estimate.

Laboratory research at Battelle-Northwest has extended the work of Yee, and has demonstrated that the use of alumina columns represents a potentially economical phosphorus removal process.

LABORATORY STUDIES

Small Alumina Columns

A synthetic secondary sewage effluent was used in the small column studies. The composition of the synthetic, to be referred to as SSE, is given in Table 3. The SSE was used as a standard influent and was

Table 3

Synthetic Secondary Sewage Effluent (pH = 7.4)

Constituent	mg/l	Constituent	mg/l
Na^{+}	130	Cl^{-}	112
K^{+}	25	HCO_3^{-}	300
NH_4^{+}	20	SO_4^{-2}	50
Ca^{+2}	60	P	3.5-10.3
Mg^{+2}	25		

compositionally altered to determine the effects of the changes on phosphorus removal by alumina.

Small, 1.1 cm diameter by 8.0 cm height columns were used with the above SSE to determine alumina phosphorus removal. The SSE was pumped through the column at a predetermined rate. Column effluent was sampled at intervals and the phosphorus content of the sample determined by the standard ammonium molybdate-aminodisulfonic acid method. The phosphorus removal values were plotted as C/C_o vs. volume of throughput where C equals the phosphorus concentration in the effluent and C_o is the phosphorus concentration in the influent.

Several investigators of alumina adsorption phenomena have considered that the adsorption is essentially a highly selective ion exchange process. With that assumption, increasing the surface area of the alumina should increase alumina phosphorus adsorption capacity. Three different columns containing aluminas of known surface area were compared as to their phosphorus capacities with the results shown in Figure 1. A simple and direct relationship between alumina surface area and phosphorus capacity was indicated. Surface area effects probably overshadowed any effects due to differences in the crystalline structure of the alumina. The boehmite

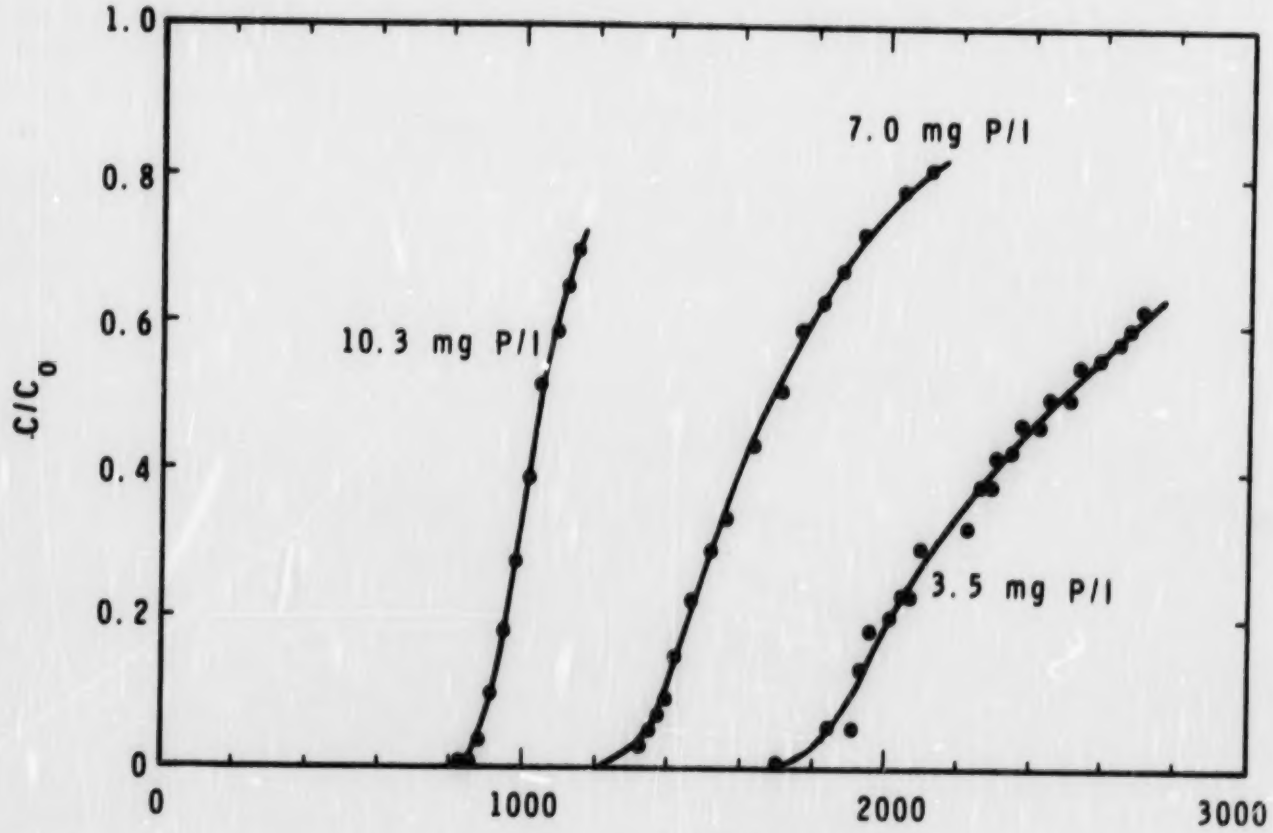


Figure 1. Phosphorus loading of aluminas of different surface areas.

Columns - A, boehmite, 22 m^2/g
B, boehmite, 200 m^2/g
C, gel, 292 m^2/g

Influent - SSE (7.0 mg P/l)

Flow Rate - 30 column volumes/hr

Temperature - 23°C

columns, for example, treated less SSE than the noncrystalline alumina, and also were less in surface area.

A rough determination of the reaction enthalpy change between 23°C and 60°C yielded a ΔH° of 15 ± 4 Kcal/mole. The ΔH° was obtained by measuring the effects of heat on the equilibrium phosphorus distribution between solution and alumina. Generally speaking, chemical reactions range upward from 20 Kcal/mole, while ion exchange reactions usually vary from 2 to 10 Kcal/mole. It may be concluded that phosphorus adsorption represents an unusually high bond strength type of ion exchange reaction.

As reported in the introduction, polyvalent anions such as phosphorus are involved in secondary adsorption reactions. Small alumina columns with varying phosphorus concentrations in the standard influent were compared as to phosphorus removal with the results shown in Figure 2. At 10% breakthrough, the throughputs for 10.3, 7.0, and 3.5 mg P/l in the standard influent were 900, 1400, and 1900 column volumes, respectively. About the same loading differences were maintained between the isotherms for other breakthrough values. If the relationship between phosphorus removal and alumina surface area were a simple one, halving the phosphorus concentration without changing the surface area should give twice the influent throughput volume to the same percent breakthrough. Since the relationship between alumina surface area and phosphorus removal obviously is not a simple inverse one, other factors such as the formation of complexes with other ions contained in the solution must be considered. The divalent cations of calcium and magnesium would be most apt to enter into complex formation with phosphorus. The effect on phosphorus removal of deleting Mg^{+2} (25 mg/l) and Ca^{+2} (60 mg/l) from the standard influent was measured with the results given in Figure 3. Phosphorus is removed from the influent containing no calcium or magnesium but the phosphorus loading is about halved when compared to a standard influent containing the usual calcium and magnesium concentrations. Most of the original phosphorus capacity is restored by the 25 mg/l of Mg^{+2}. At least part of the phosphorus is bonded onto the alumina surface by a complex involving Mg^{+2} and Ca^{+2}. As the phosphorus concentration increases, the portion of the phosphorus removed by this

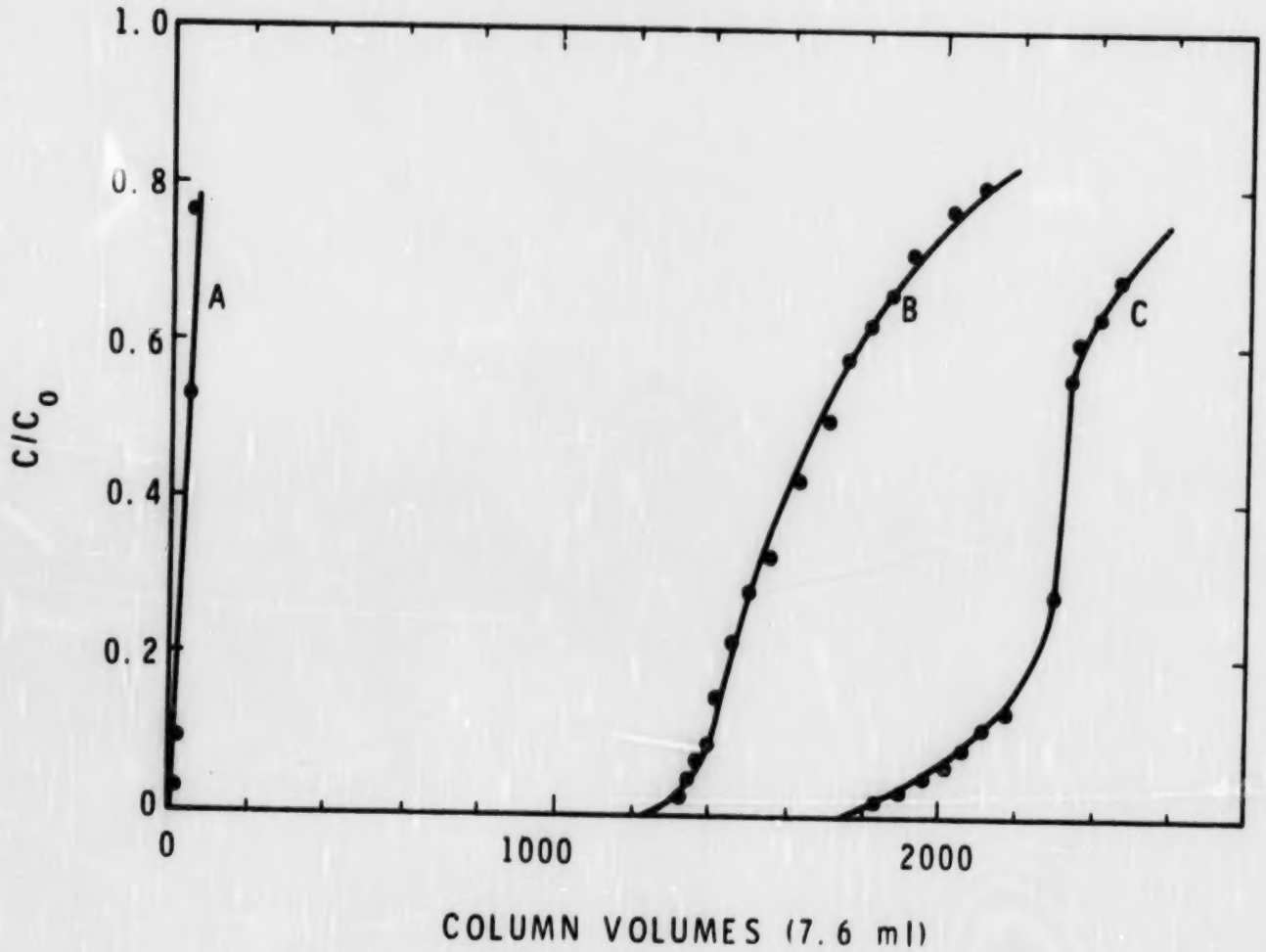


Figure 2. Effects of phosphorus concentration on phosphorus removal by alumina.

Columns - Boehmite, 100 to 200 mesh

Influent - SSE with P content as indicated

Flow Rate - 30 column volumes/hr

Temperature - 23°C

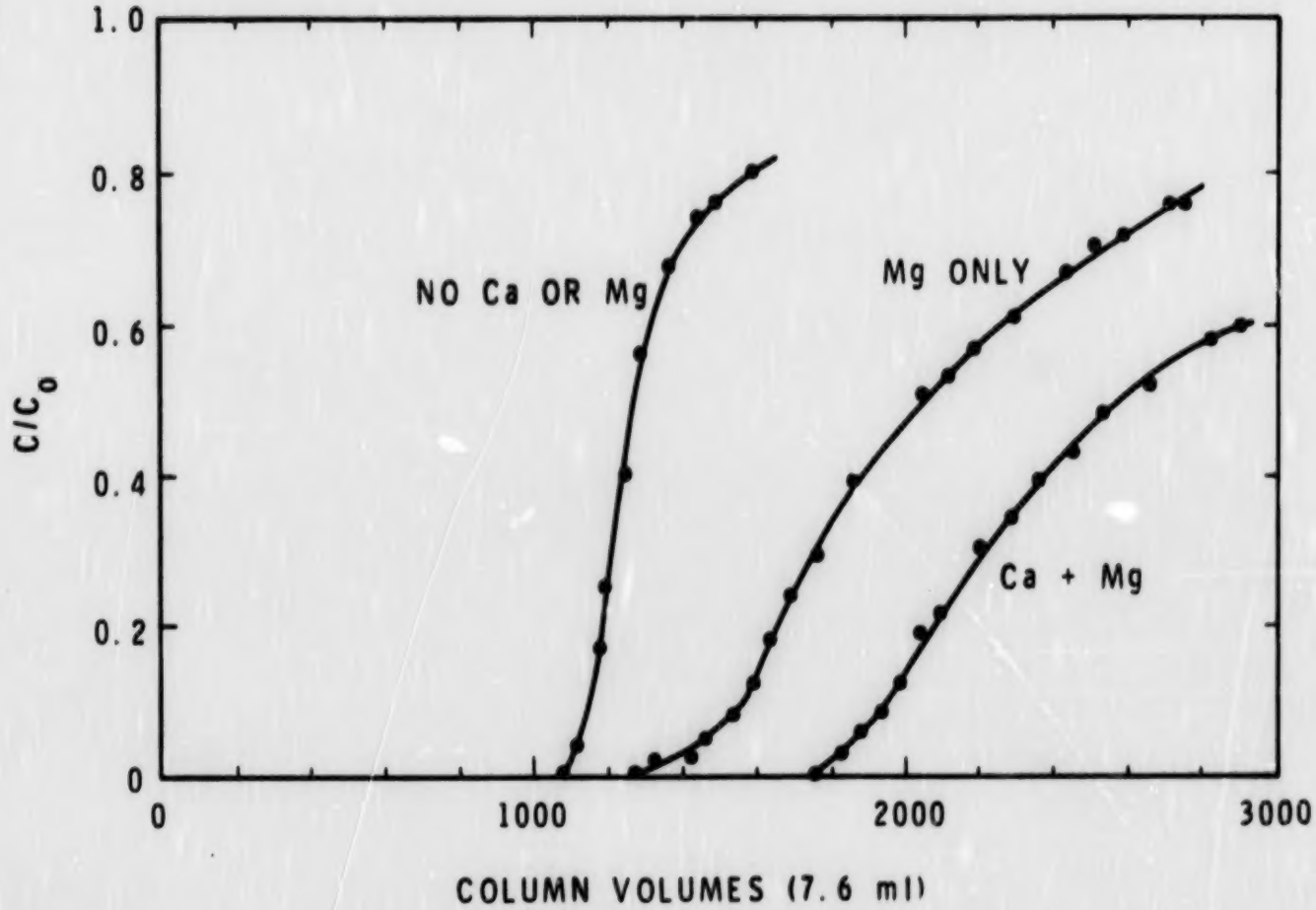


Figure 3. Effects of calcium and magnesium ions on phosphorus removal by alumina.

Columns - Boehmite, 100 to 200 mesh

Influent - SSE (3.5 mg P/1)

Flow Rate - 30 column volumes/hr

Temperature-23°C

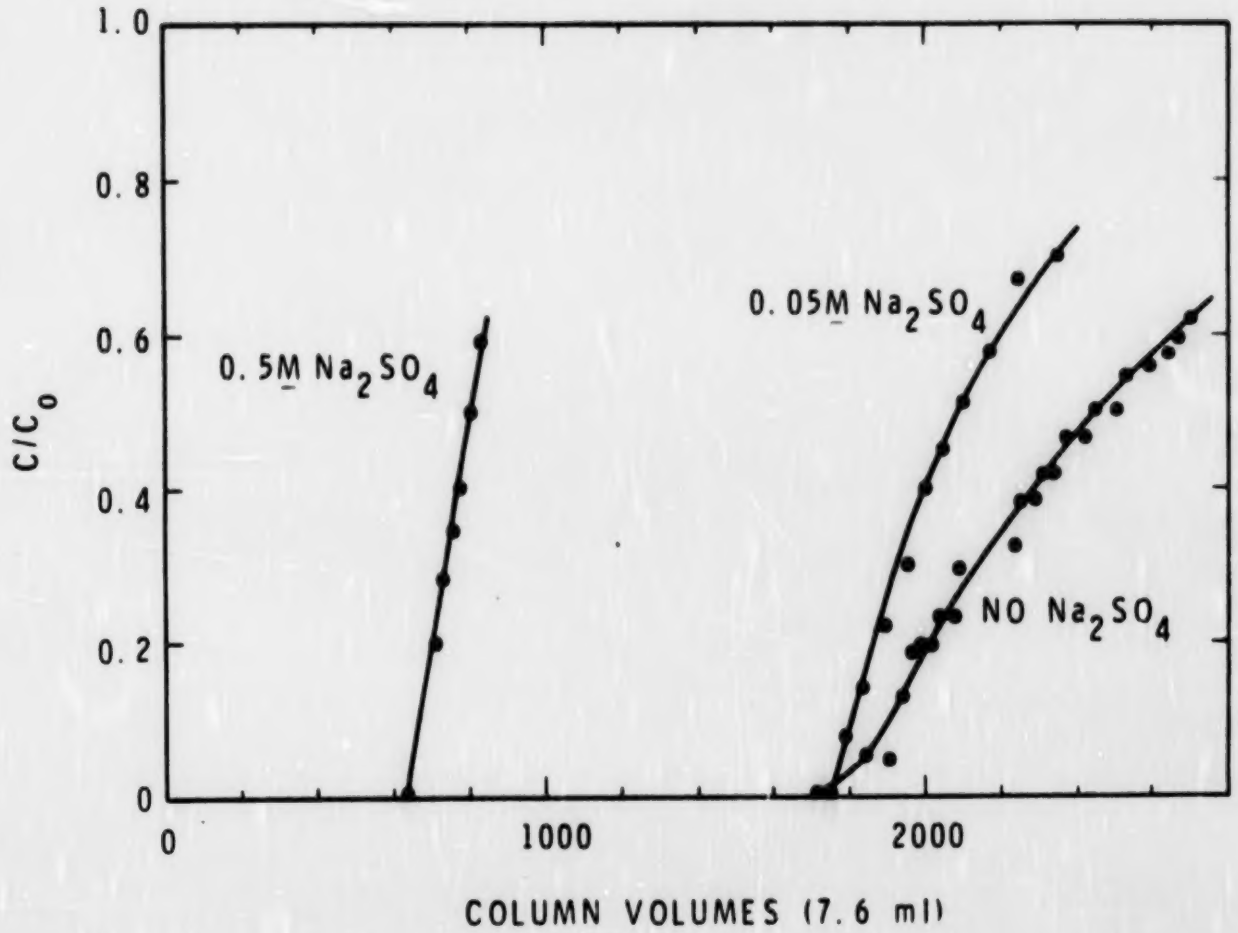
complex may increase, giving larger phosphorus removal values than could be expected from a consideration of alumina surface area alone.

The competition, or effects of other anions on phosphorus removal was of interest because large concentrations of other anions could significantly lower the alumina phosphorus capacity. Sulfate ion was chosen to demonstrate phosphorus capacity effects due to some similarities in the behavior of SO_4^{-2} and HPO_4^{-2}. The phosphorus loading curves from a simulated secondary sewage effluent containing 3.5 mg P/l are shown in Figure 4. Unusually large concentrations of sulfate ions are necessary to adversely affect phosphorus removal by the boehmite. This conclusion is probably valid for other anions with the exception of arsenate. $HAsO_4^{-2}$ could be expected to substitute for HPO_4^{-2} in the adsorption reaction with little difference in alumina selectivity between the two anions.

Though the aluminas used in the study were all high in surface area, grain size still had an effect on the efficiency of phosphorus removal.

Assuming a normal distribution within size ranges and a spherical shape, the 10 to 20 mesh range should have a surface area of less than 1 m^2/g and the 48 to 100 mesh somewhat larger. A B.E.T. surface area, however, results in values of 290 m^2/g for both size ranges of alumina gel. The same high surface area is available for all gel size ranges and all sizes would remove the same amount of phosphorus if equilibrium between phosphorus and solution were attained. The effects of size range on phosphorus loading characteristics seen in Figure 5 are due to the kinetics of phosphorus diffusion from the solution surrounding the alumina particle, through the particle to the adsorption site.

Diffusion kinetics[6] for exchange reactions are of two types; particle diffusion and film diffusion. Particle diffusion is so-called because diffusion of the exchanging ions from alumina particle surface into the particle is the rate-determining step. Particle diffusion assumes a high concentration of the exchanging ions in the solution surrounding the alumina particle. If the size of the exchanging ions is very large, however, the concentration of ions in the solution can be quite low and still have particle diffusion. Film diffusion is so-named because diffusion of the exchanging ions within the particle is very fast, leading to depletion



Figur : 4. Phosphorus loading curves from standard secondary sewage effluent containing varying amounts of sodium sulfate.

Columns - Boehmite, 8g

Influent - SSE (3.5 mg P/l)

Flow Rate - 30 column volumes/hr

Temperature - 23°C

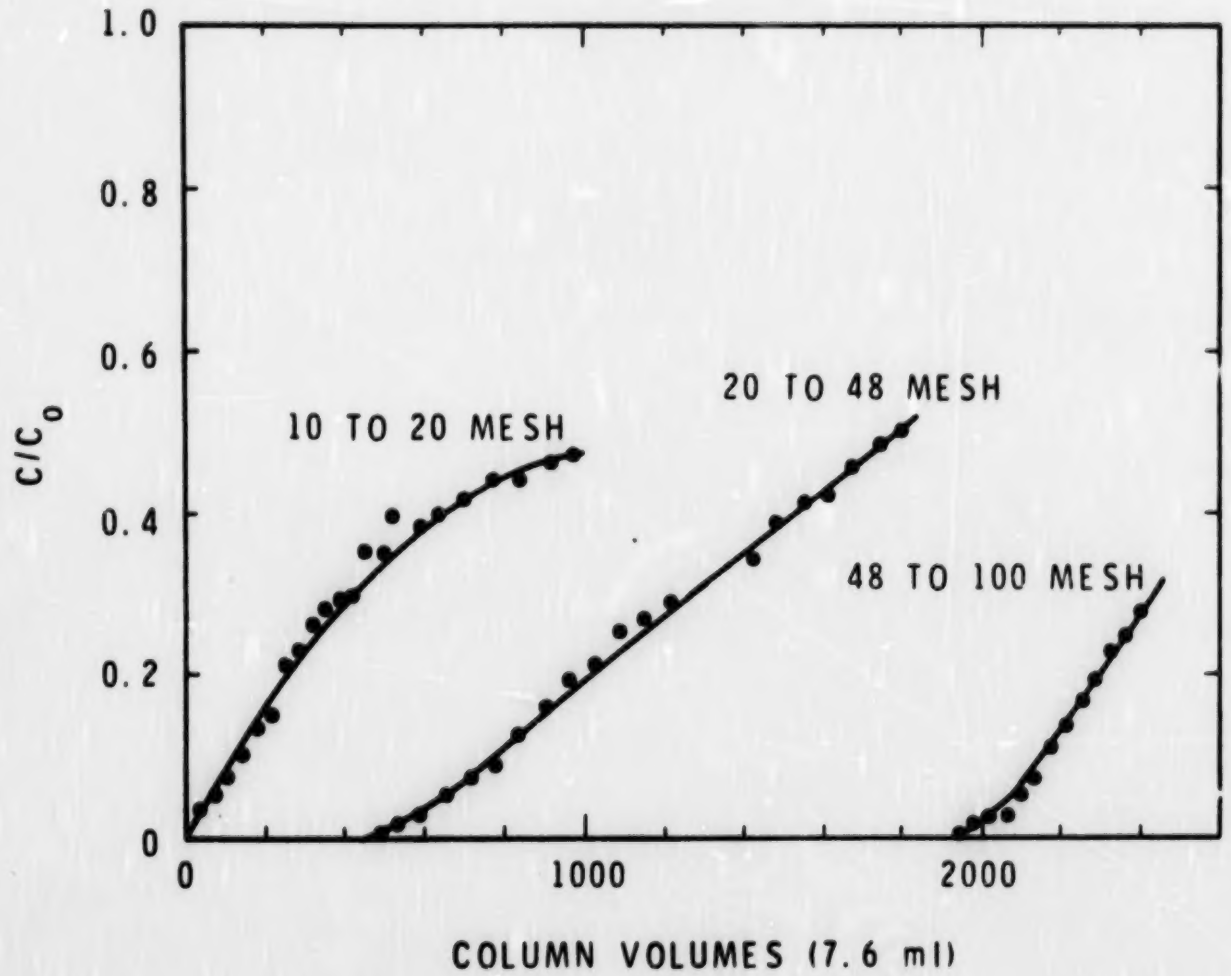


Figure 5. Effect of grain size range on phosphorus adsorption kinetics. Sieve dimensions are U.S. Standard Series.

Columns- Alumina gel, mesh sizes as indicated, surface area = 290 m^2/g

Flow Rate - 35 column volumes/hr

Temperature - 23°C

Influent - SSE (6.7 mg P/l)

of these ions in a film of solution surrounding the alumina particle. Diffusion of ions across the film surrounding the particle is the rate-determining step. The concentration of exchanging ions in the solution is usually low. The diffusion time necessary to attain a given fraction of equilibrium loading varies inversely as the square of the particle radius in the case of particle diffusion, and by a simple inverse ratio to particle radius in the case of film diffusion. From a consideration of the curves shown in Figure 5, it is probable that particle diffusion is rate controlling, despite the low concentrations of phosphorus. More elaborate techniques are required, however, to verify the rate controlling step.

Elution of SSE phosphorus loaded columns with various strength acidic solutions and sodium sulfate is shown in Figure 6. Elution rates fell off rapidly and were generally inefficiently slow. In addition, acidic elutions left the column in a condition that was detrimental to phosphorus reloading. A 1N H_2SO_4 alumina column prewash resulted in 2 to 5% phosphorus leakage and reduced phosphorus loading as shown in Figure 7.

Basic elutions are recommended both because they are more efficient and do not reduce the following phosphorus reloading. Sodium hydroxide and sodium carbonate phosphorus elution curves are given in Figure 8. The sodium carbonate elution rate is slower than that of sodium hydroxide. Both of the curves of Figure 8 represent elution of a first cycle loading alumina column, and illustrate that diffusion of hydroxide ion into the alumina particle, and phosphorus out of the particle requires considerable time. More time is required to regenerate the last 20% of the alumina phosphorus capacity than the duration of the elution afforded.

A leaching experiment with 1M NaOH and boehmite and alumina gel was conducted to obtain a feeling for alumina losses during sodium hydroxide elutions. Losses would occur mainly during elution because alumina solubility in solutions such as SSE is very low. Excessive losses of alumina during elution would moreover, adversely affect wastewater treatment costs. Eight gram columns of 16 to 60 mesh alumina gel and 100 to 200 mesh boehmite were leached for several days at a flow rate of 30 column volumes/hr with 1M NaOH. The dissolution rate of alumina gel was 6.3 wt%/24 hrs and for boehmite, 1.2 wt%/24 hrs. The above weight losses may be compared to Yee's

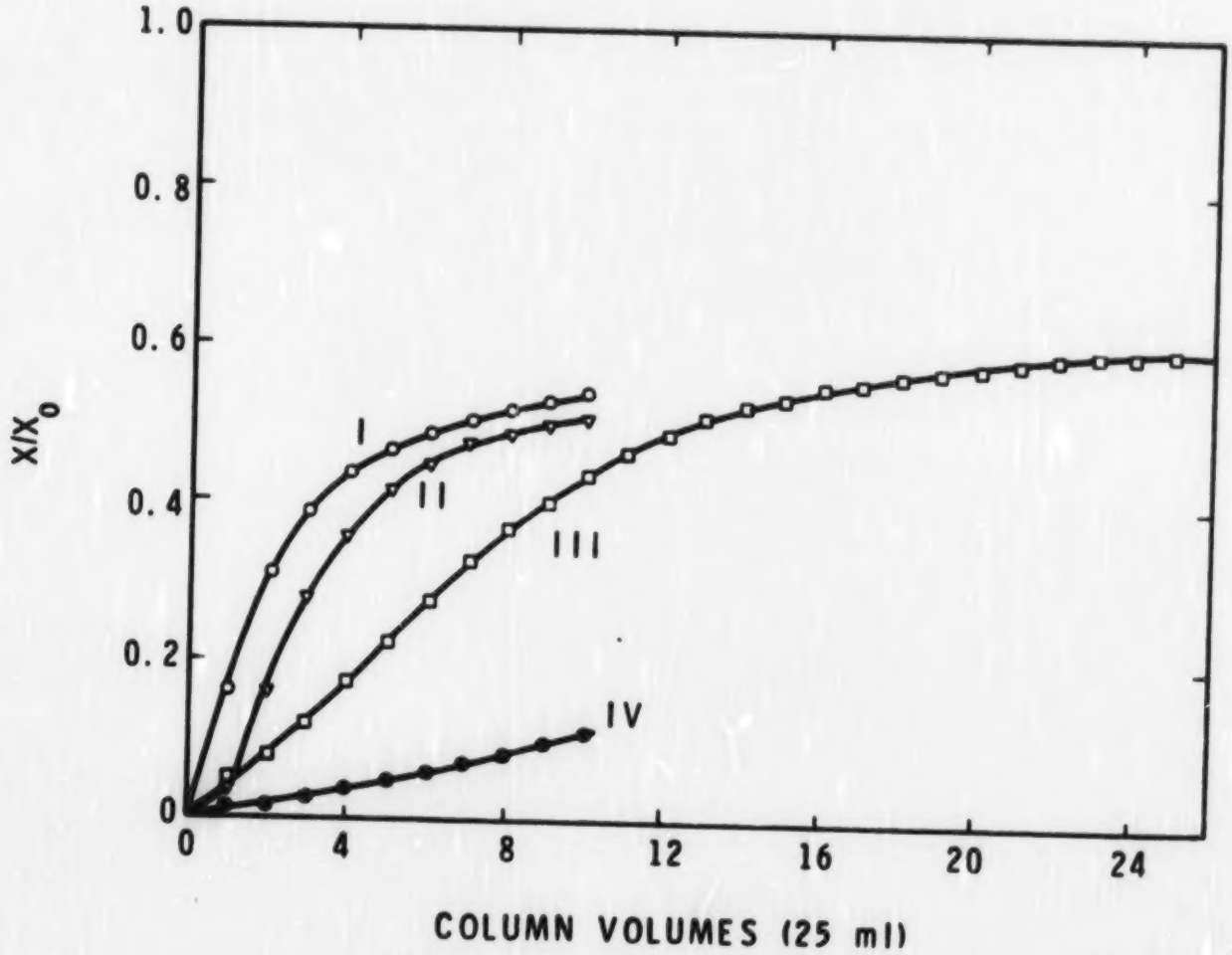


Figure 6. Alumina phosphorus elution curves. X/X_o is the fraction of P removed from the column by the elution treatment.

Column - Boehmite, 100 to 200 mesh

Flow Rate - 35 column volumes/hr

Temperature - 23°C

I - eluted with 1.0N H_2SO_4, C_o = 257 mg P

II - eluted with 0.5N H_2SO_4, C_o = 296 mg P

III - eluted with 0.1N H_2SO_4, C_o = 269 mg P

IV - eluted with 2.0N Na_2SO_4, C_o = 272 mg P

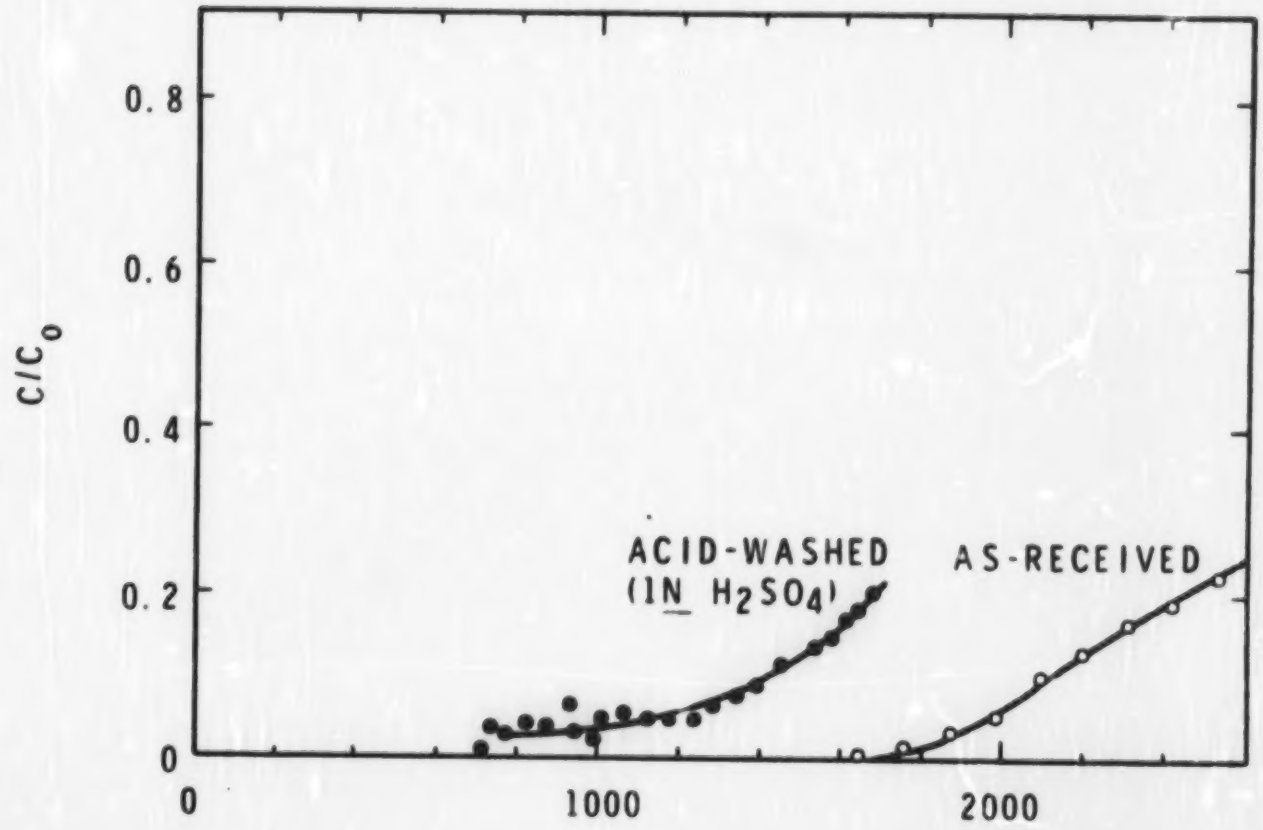


Figure 7. Effect of acid washing of alumina on subsequent phosphorus reloading.

Column - Boehmite, minus 100 mesh

Flow Rate - 30 column volumes/hr

Temperature - 23°C

Influent - SSE (7.5 mg P/l)

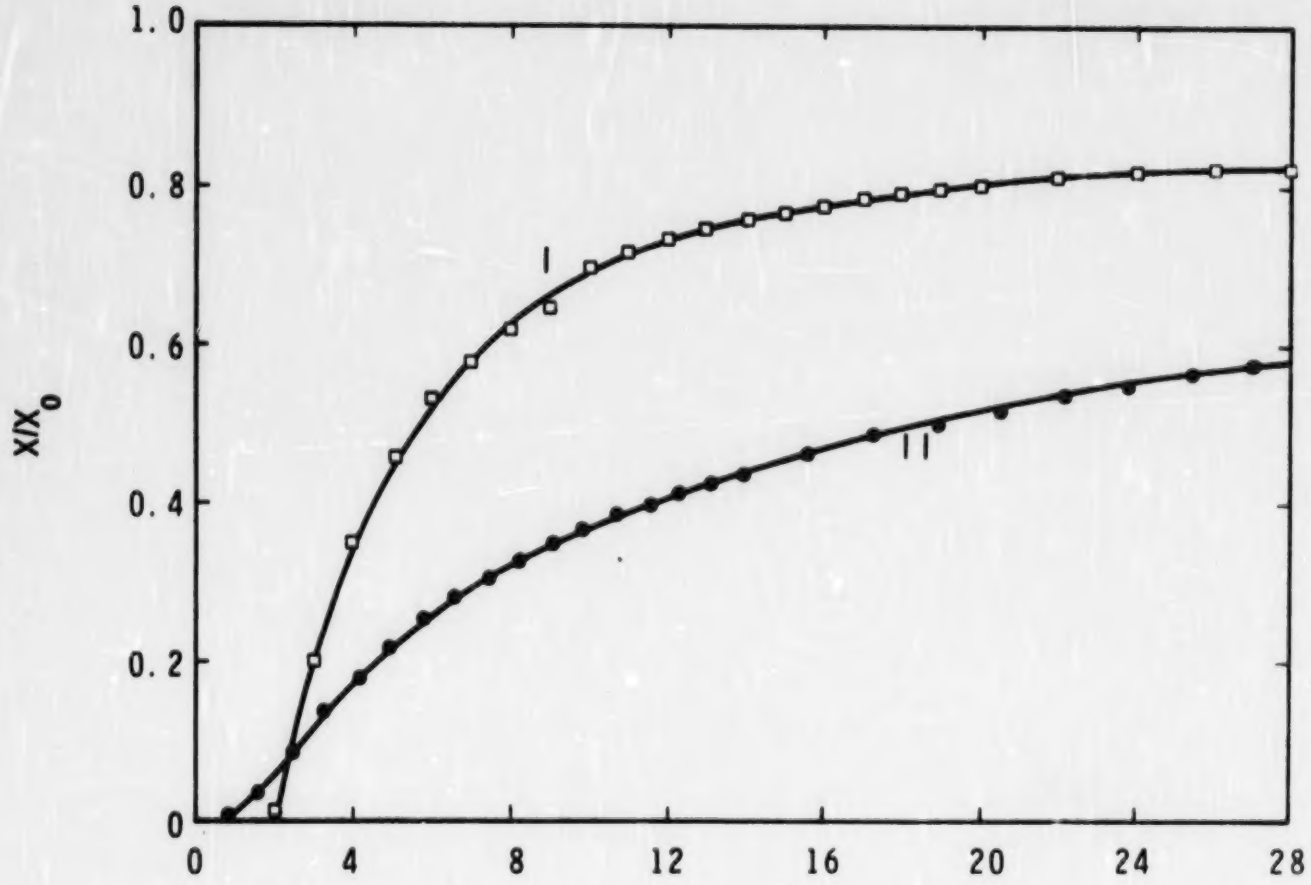


Figure 8. Sodium carbonate and sodium hydroxide phosphorus elution curves. X/X_0 is the fraction of P removed from the column by the elution treatment.

Columns - Boehmite, 100 to 200 mesh, 200 m^2/g

Flow Rate - 30 column volumes/hr

Elution Solutions - I. 1M NaOH, C_o = 74.6 mg P

II. 1M Na_2CO_3, C_o = 54.7 mg P

reported losses of 8% per elution for boehmite and up to three or four times the 8% loss for alumina glass. Although the weight loss ratio is the same as that of this study, the lower losses here probably reflect leaving out the acid step in regeneration.

If sodium hydroxide is to be used as an alumina column regenerant, some method of disposal or reuse must be found for the spent regenerant solution. Lime represented a possible cheap solution to the problem by removing phosphorus and carbonate from the spent regenerant sodium hydroxide. Equilibrium results with phosphorus removal from one and five molar sodium hydroxide solutions by lime were ascertained as shown in Figures 9 and 10. A 0.1137 molar disodium acid phosphate was used because the most concentrated phosphorus solution obtained early in the elution step is approximately of this composition. The hypothetical tricalcium phosphate line was added for comparative purposes only. The phosphorus is precipitated as a hydroxyapatite. An apatite is also the raw natural material used in making fertilizer and phosphorus chemicals. The monetary value of the apatite produced would probably be very small.

In any case, increments of lime were added to 100 ml solutions containing the milligrams of phosphorus indicated in Figures 9 and 10. Some of the samples were shaken for 15 minutes and some for an hour, with the same concentration of phosphorus remaining in the solution. A rapid lime-solution reaction was indicated. The solids filtered from these mixtures were identified by X-ray diffraction as lime and hydroxyapatite. No extraneous anions were added to the sodium hydroxide regenerant solution by the lime, and CO_3^{-2}, originally HCO_3^- before elution, also was removed. Less than 30 mg SO_4^{-2}/l and 1 mg Cl^-/l were found in a regenerant solution that had been reused 10 times.

Some alumina column fouling with calcite ($CaCO_3$) occurred during loading with high pH synthetic secondary sewage effluents. For several consecutive cycles of loading and sodium hydroxide elution, the results are seen in Figure 11. Note that alumina column phosphorus capacity steadily declines for each successive cycle. An alumina sample removed from the column for X-ray diffraction study showed the presence of calcite

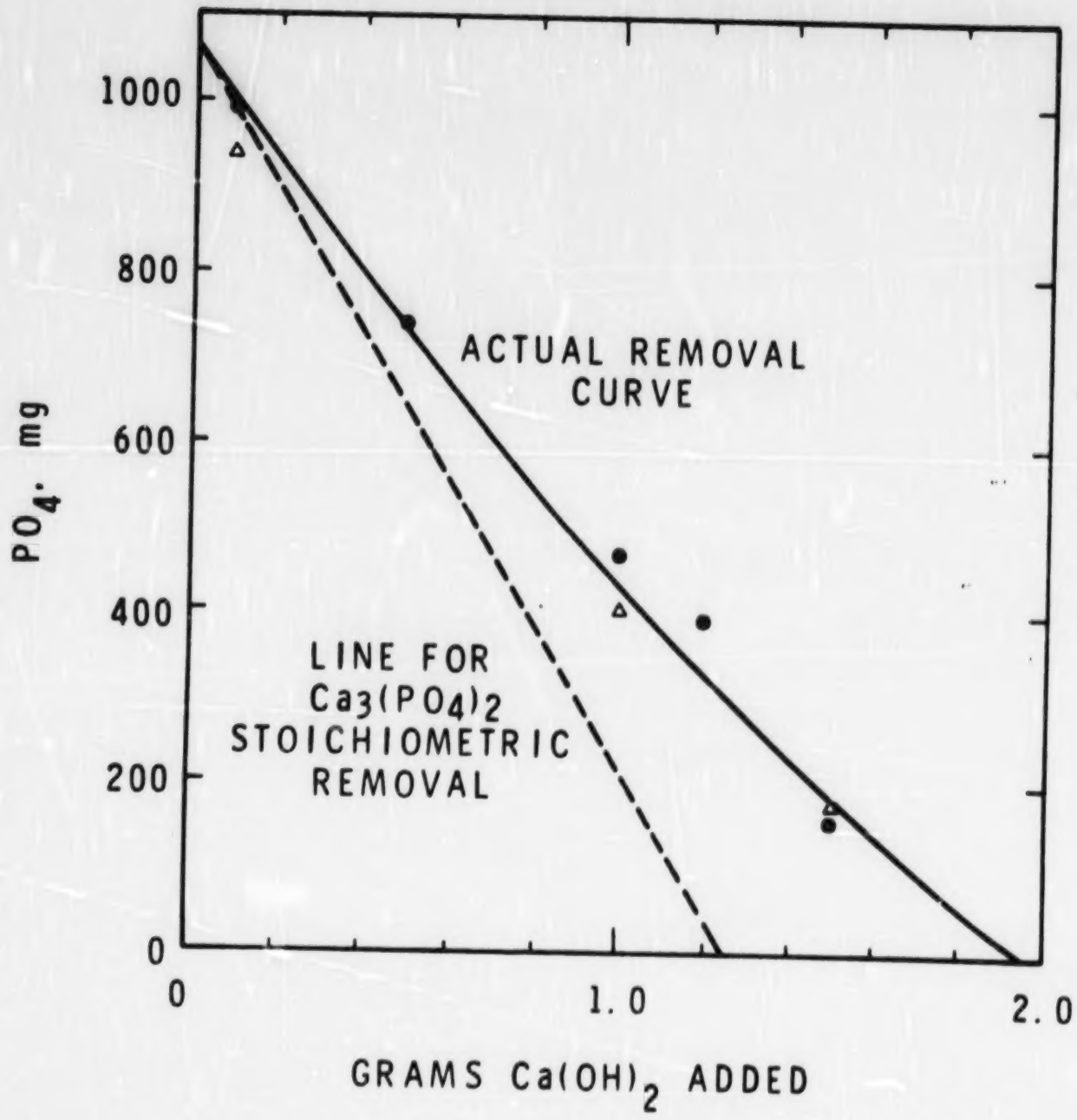


Figure 9. Equilibrium phosphorus removal results when $Ca(OH)_2$ was added to 100 ml of a 1.0M NaOH + 0.1137M Na_3PO_4 solution.

Δ = 15 minutes equilibration time

• = 1 hr equilibration time

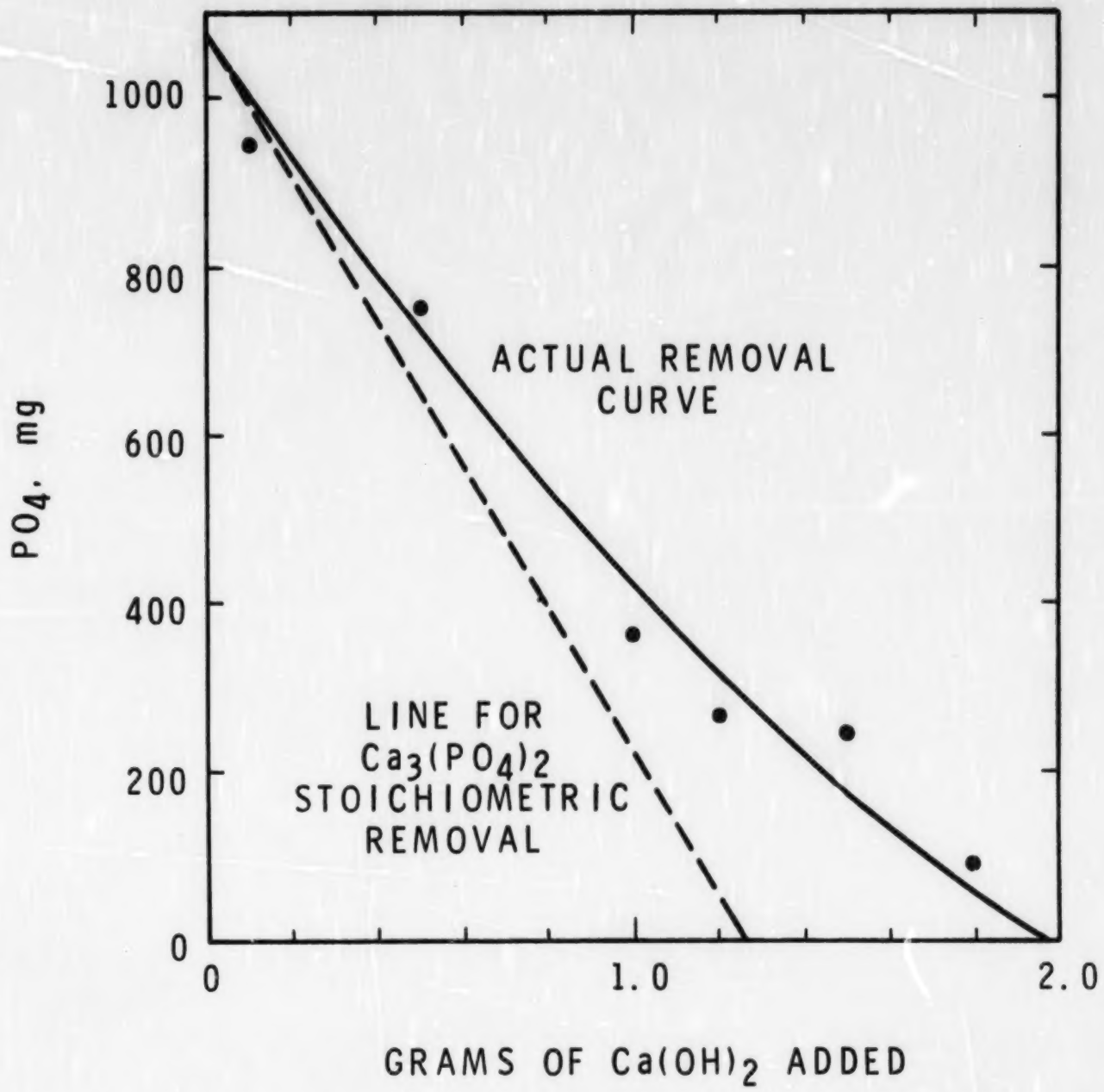


Figure 10. Equilibrium phosphorus removal results when $Ca(OH)_2$ was added to 100 ml of a 5.0M NaOH + 0.1137M $Na_3 PO_4$ solution.

• = 1 hr equilibration time

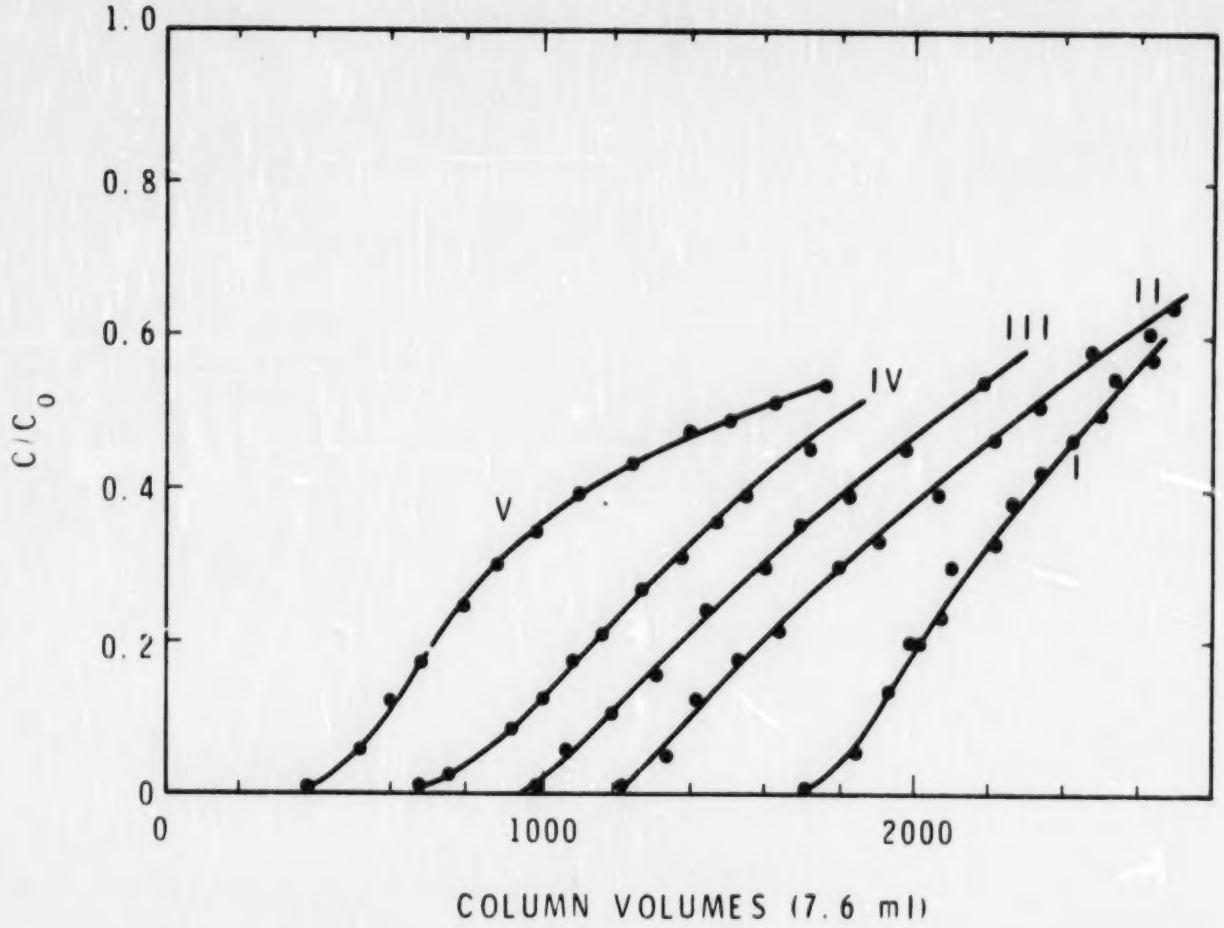


Figure 11. Effect on alumina phosphorus capacity of progressive calcitic grain coating.

Column - Boehmite, 100 to 200 mesh

Flow rate - 30 column volumes/hr

Temperature - 23°C

Influent - SSE (6.7 mg P/l), pH = 8.2

Elution - 1.0M NaOH

Cycles - As indicated

coating the alumina grains. This precipitation of calcite on the alumina lowers the alumina surface area available for phosphorus adsorption, and calcite is not removed from the column during elution with sodium hydroxide. As alumina grains became calcite-coated, phosphorus surface adsorption was effectively blocked. Several ways are available to treat the calcite problem. One way is to leach the column with a bicarbonate solution. The restoration of a calcitic alumina column is shown in Figure 12. Nearly all of the phosphorus capacity was regained after $NaHCO_3$ solution was recirculated through the column. Lime can be added to the phosphorus-containing $NaHCO_3$ to precipitate apatite, if an excess of lime is avoided. The $NaHCO_3$ solution can then be reused. It is still necessary to remove any alumina-adsorbed phosphorus with NaOH. The problem of calcite imbalance was not encountered with actual secondary sewage effluent from the Richland trickling filter plant.

If Richland effluent is used to load both the large (one liter) and small (6.7 ml) columns, the resulting phosphorus breakthrough curves are very similar. However, if the Richland effluent breakthrough curve is compared to the phosphorus breakthrough curve of the SSE on the same size column, the results are considerably different as shown in Figure 13. The SSE can not really represent a synthetic secondary sewage effluent, in terms of total alumina phosphorus capacity at least. Even though the phosphorus capacity of the alumina is reduced when Richland effluent is used for loading, the characteristic reactions of alumina are the same in each case, as will be shown later. The small column-SSE work is therefore useful in predicting how the alumina will react to given loading and elution conditions. The small column-SSE work is not useful for predicting phosphorus capacities of alumina when actual sewage effluents are used for loading.

One Liter Alumina Columns

The composition of Richland trickling filter effluent used as the influent in the one liter column studies varied over the range given in Table 4. One liter alumina columns (5.1 cm diameter by 49 cm high) were used with Richland effluent to determine the effects of elution method on

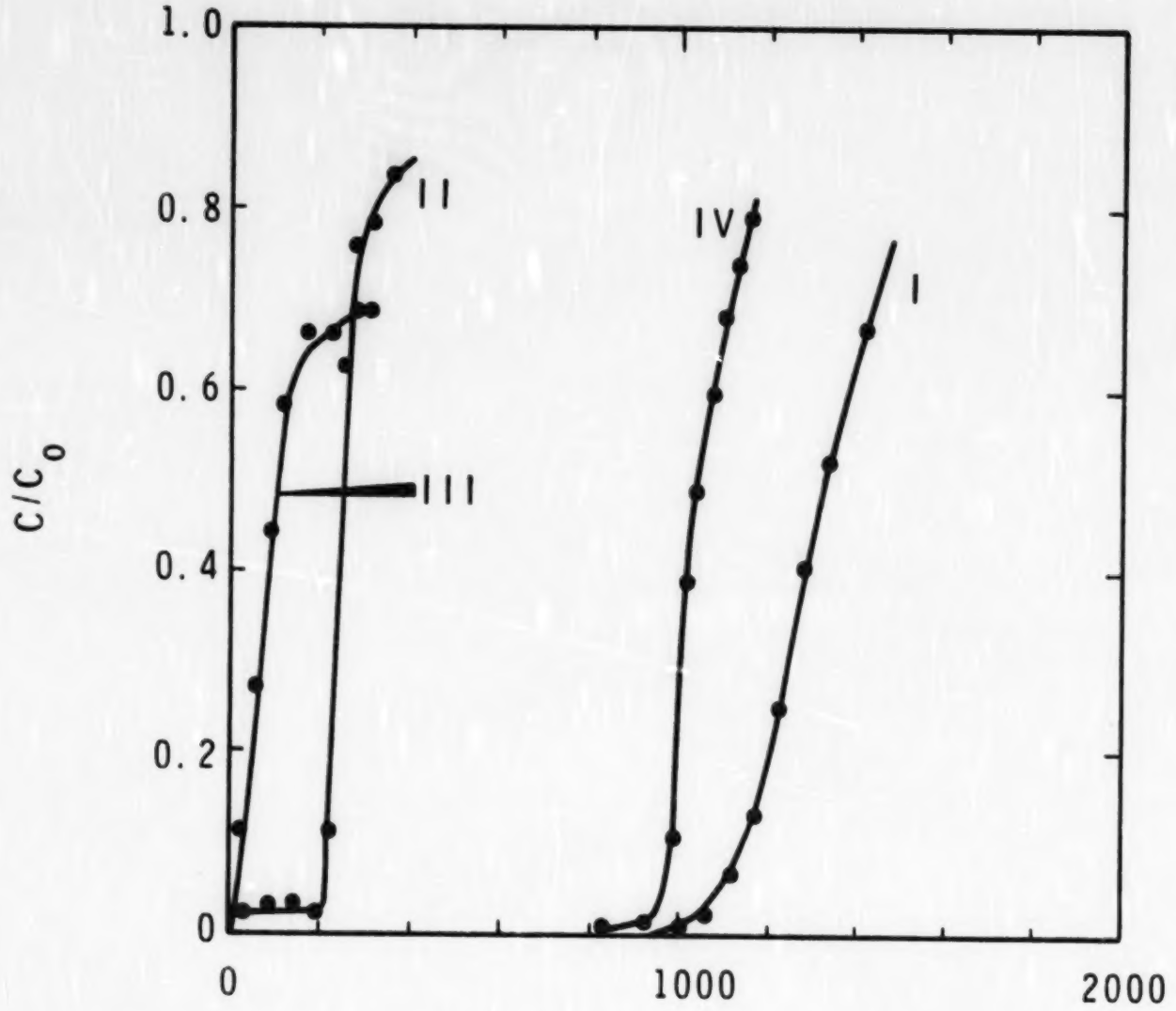


Figure 12. Restoration of calcitic alumina column phosphorus capacity with $NaHCO_3$ following loading Cycle III.

Column - Boehmite, 100 to 200 mesh

Flow Rate - 30 column volumes/hr

Temperature - 23°C

Cycles - As indicated

$NaHCO_3$ Concentration - 1.0M $NaHCO_3$

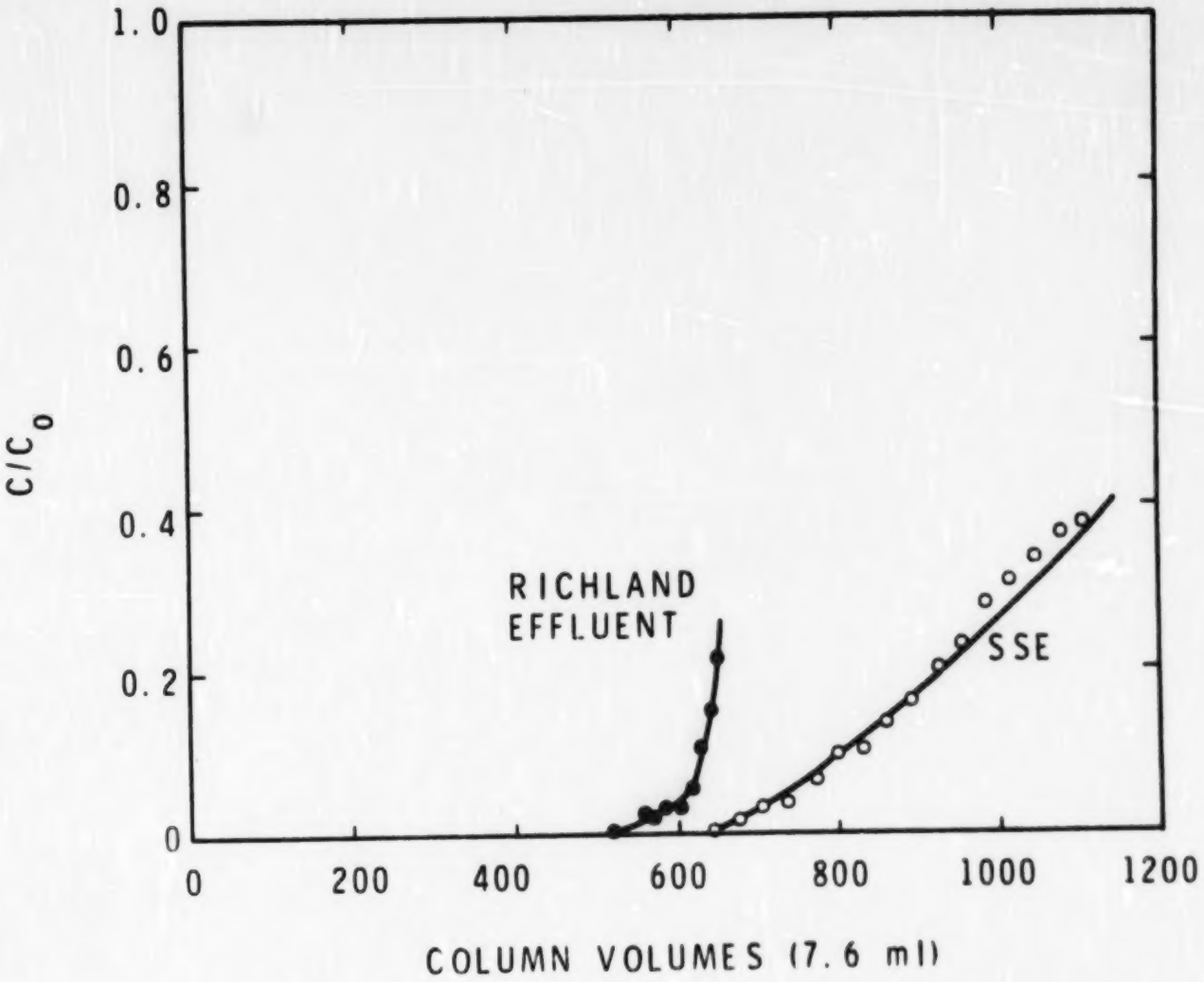


Figure 13. Comparison of SSE (10 mg P/l) and Richland effluent (10 mg P/l) phosphorus loading curves.

Columns - Alumina, 20 to 48 mesh

Flow Rate - 15 column volumes/hr

Temperature - 23°C

Table 4

Richland Secondary Effluent Composition

Constituent	mg/l range
Na^+	40-60
K^+	12-15
NH_4^+	10-14
Mg^{++}	6-9
Ca^{++}	25-40
NO_3^-	11
PO_4^{-3}	25-35
Alkalinity as $CaCO_3$ equivalent	180-190
pH	7.2-7.8

subsequent phosphorus reloading. The Richland sewage effluent was stored outside in a covered 500 gallon polyethylene tank. The effluent was pumped inside and degassed by heating to room temperature and passed through a 7.6 cm diameter by 60 cm granulated charcoal column before going to the alumina.

The one liter alumina column loading data are given in Figure 14. Note that there is an initial drop in capacity going from Cycle I to Cycle II, as there was when SSE was used as an influent. Various elution treatments were tried following each cycle to ascertain the effects, if any, on the following loading cycle. Ten column volumes of 1M NaOH were used to elute the column after loading Cycles I and II. Saturated $Ca(OH)_2$ solution was tried as an eluting agent following loading Cycles III and IV. The phosphorus capacity fell steadily for the following loading Cycles IV and V. The precipitation of solids in the alumina bed was observed. Recovery and X-ray diffraction of a sample of the solids showed that they were mostly calcite and a little apatite. A gram of the precipitated solid contained 23 mg of phosphorus. As the alkalinity of the Richland effluent implies, it must contain about 115 mg HCO_3^-/l. Since the alumina can adsorb part of this HCO_3^-, as well as the phosphorus, the $Ca(OH)_2$ solution must immediately precipitate calcite (and apatite) within the column and on the alumina grains resulting in reduced phosphorus adsorption capacity.

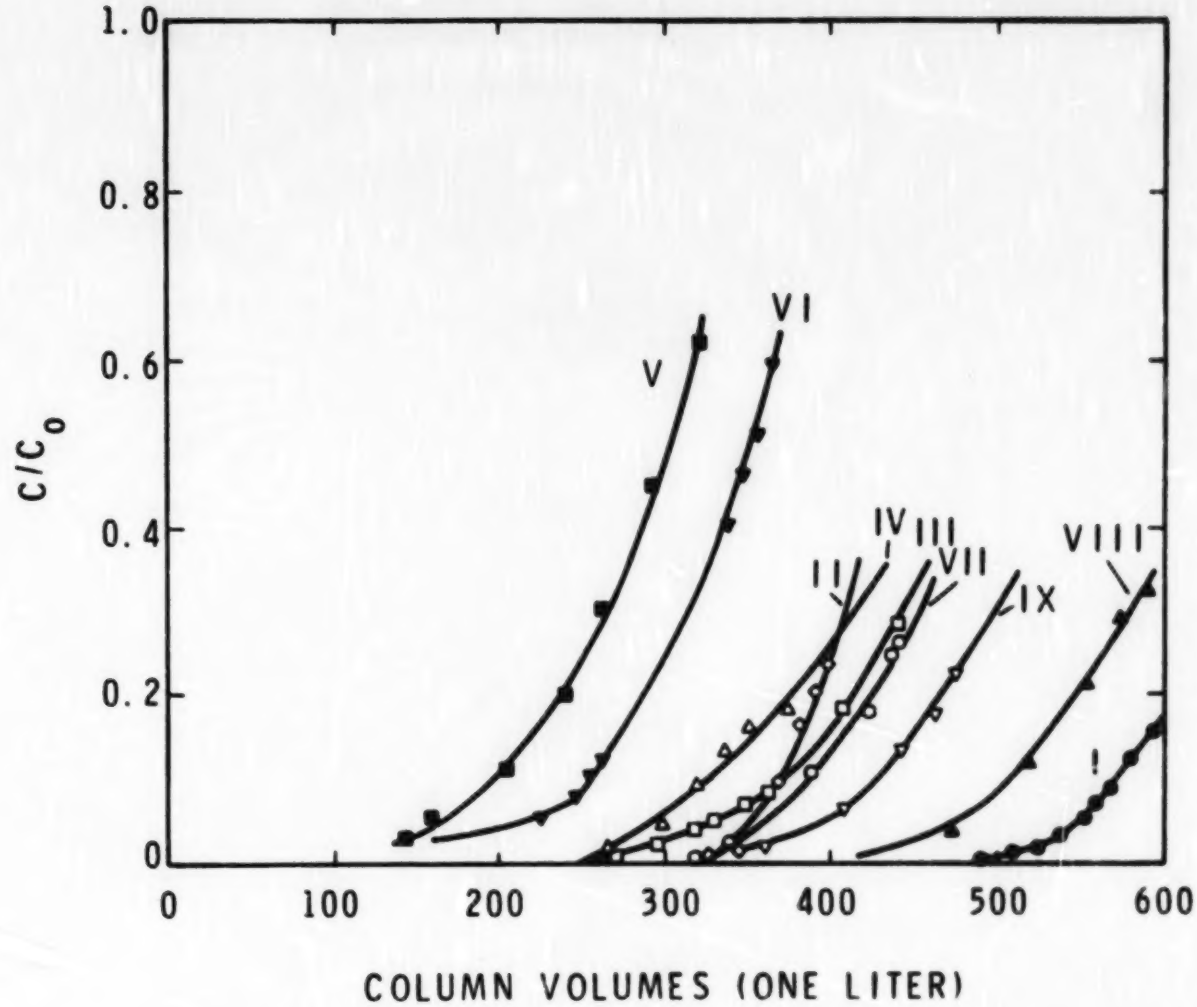


Figure 14. Comparison of consecutive phosphorus loading curves for a variously-regenerated two inch alumina column.

Column - Alumina, 20 to 48 mesh
Influent - Richland secondary effluent (10.3 mg P/1)
Flow Rates - Cycles I, II, and III - 15 column volumes/hr;
Cycles IV through IX - 5 column volumes/hr
Temperature - 23°C
Elution Treatment - I, 10 1 1M NaOH; II, 10 1 1M NaOH; III, 50 1 sat. $Ca(OH)_2$ solution; IV, 50 1 sat. $Ca(OH)_2$ solution; V, 15 1 10% HCl; VI, 12 1 2M NaOH; VII, 16 1 2M NaOH; VIII, 8 1 2M NaOH. Elution treatments followed above-associated loading cycle numbers.

An elution curve after Cycle III loading is given in Figure 15. The hydroxide from the saturated $Ca(OH)_2$ solution is able to elute the adsorbed phosphorus, and is removed from the solution in the process. The effluents from the elution contained very little phosphorus because the bulk of it was precipitated in the column along with calcite.

An acid wash after Cycle V contained 8.4 g of phosphorus in 15 liters. The following loading, Cycle VI, showed low capacity because acid is a poor phosphorus eluting agent and acid treatment of alumina, as shown by previous work, results in lowered phosphorus capacity. A regeneration with 2M NaOH following loading Cycle VI resulted in restoration of the column to normal phosphorus operating capacity (400 column volumes of Richland effluent to 10% breakthrough). Nearly twice as much phosphorus was eluted after loading Cycle VI as was loaded on the column by Cycle VI. The extra phosphorus was left over from an incomplete elution with HCl after loading Cycle V. Nearly all of the phosphorus loaded during Cycle VII was removed by the 2M NaOH elution following Cycle VII. The two molar solution was used because all of the biodegradable material was not removed by the charcoal column, resulting in formation of a bacterial colony about 2 cm deep on the top of the downflow column. This cap seemed to be more easily removed by the 2M NaOH. The 1M NaOH was made up to 2M NaOH and reused a total of four times with good results.

Elution of Cycle VIII loading was accomplished with eight column volumes of 2M NaOH. The column was drained before elution to avoid contamination of the NaOH by Richland effluent, and drained after elution to cut NaOH losses. The column then was washed with tap water. The phosphorus content of the various wash solutions is given in greater detail in Figures 16 and 17. The phosphorus content is indicated on one scale and pH on an opposite scale.

The high phosphorus washwater through 20 column volumes varies over the range 83 mg to 10 mg P/l. The rest of the wash ranges between 10 mg and 1.2 mg P/l and is relatively low in pH.

For the first eight phosphorus loading cycles on the one liter column, charcoal-filtered Richland effluent was used as the influent to reduce the biodegradable materials applied which might interfere with phosphorus removal.

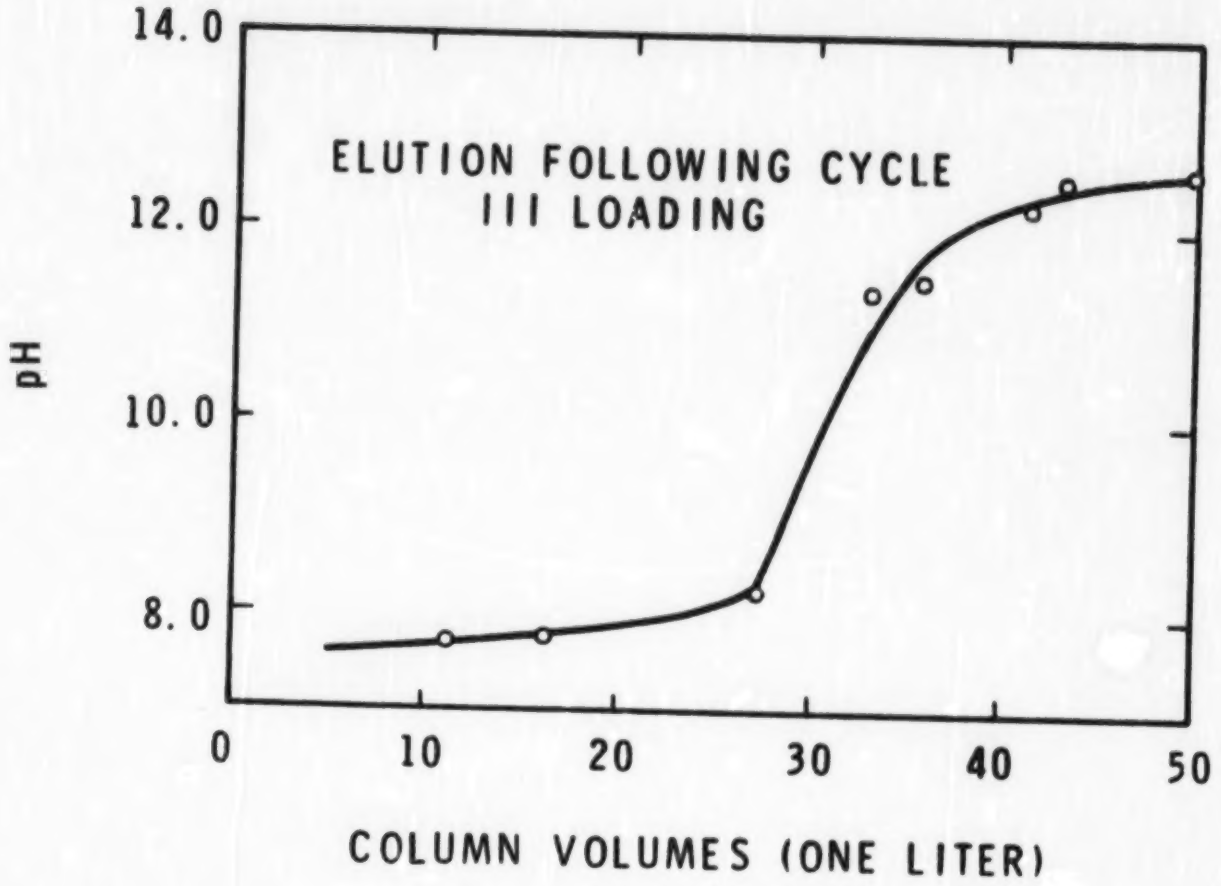


Figure 15. Elution of the two inch alumina column with saturated $Ca(OH)_2$ solution.

Column - 20 to 48 mesh alumina loaded with P from Richland secondary effluent

Flow Rate - 6 column volumes/hr

Temperature - 25°C

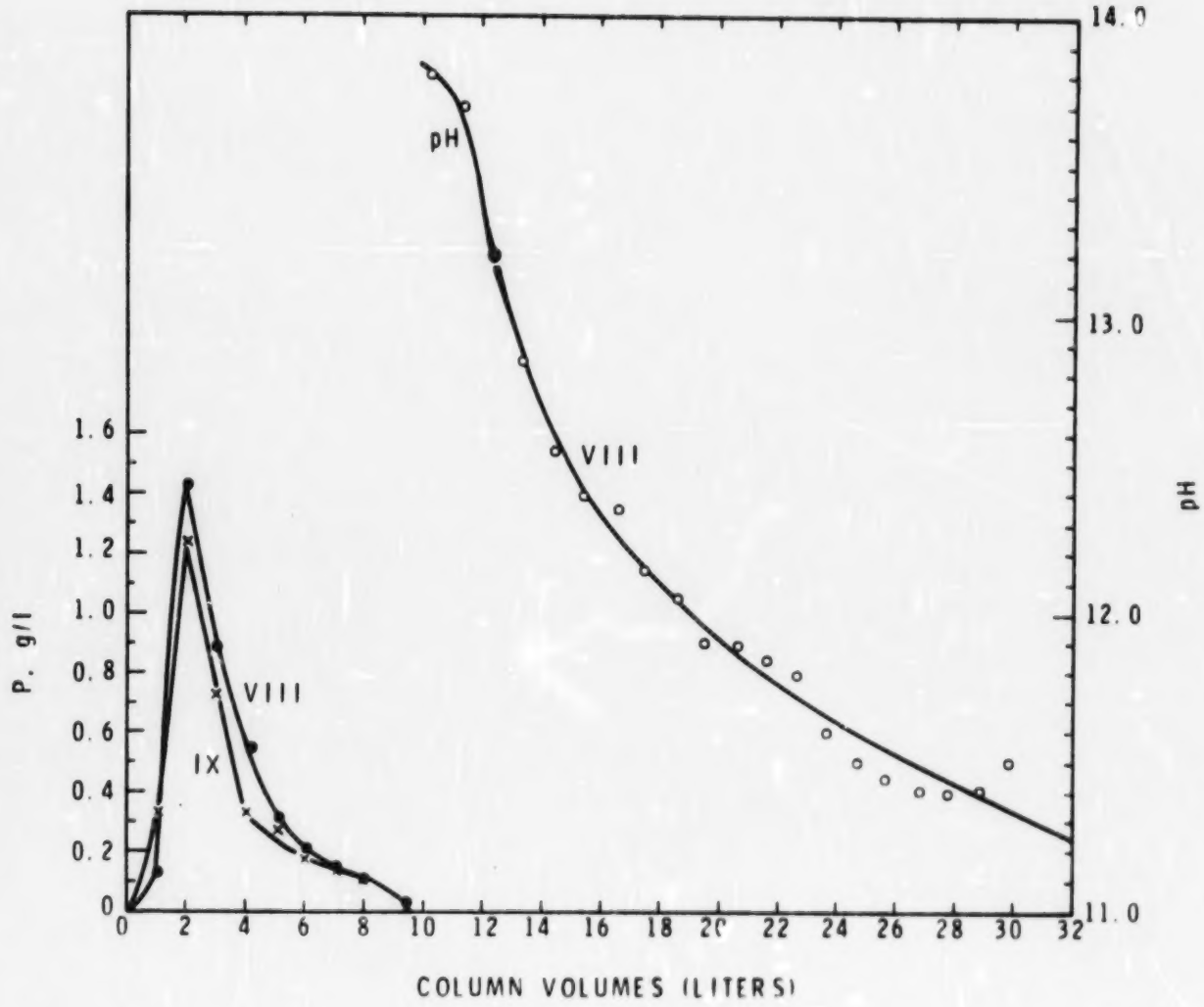


Figure 16. Elution of the two inch alumina column with NaOH following loadings VIII and IX.

Column - 20 to 48 mesh alumina loaded with Richland effluent

Flow Rate - 6.1 column volumes/hr

Temperature - 23°C

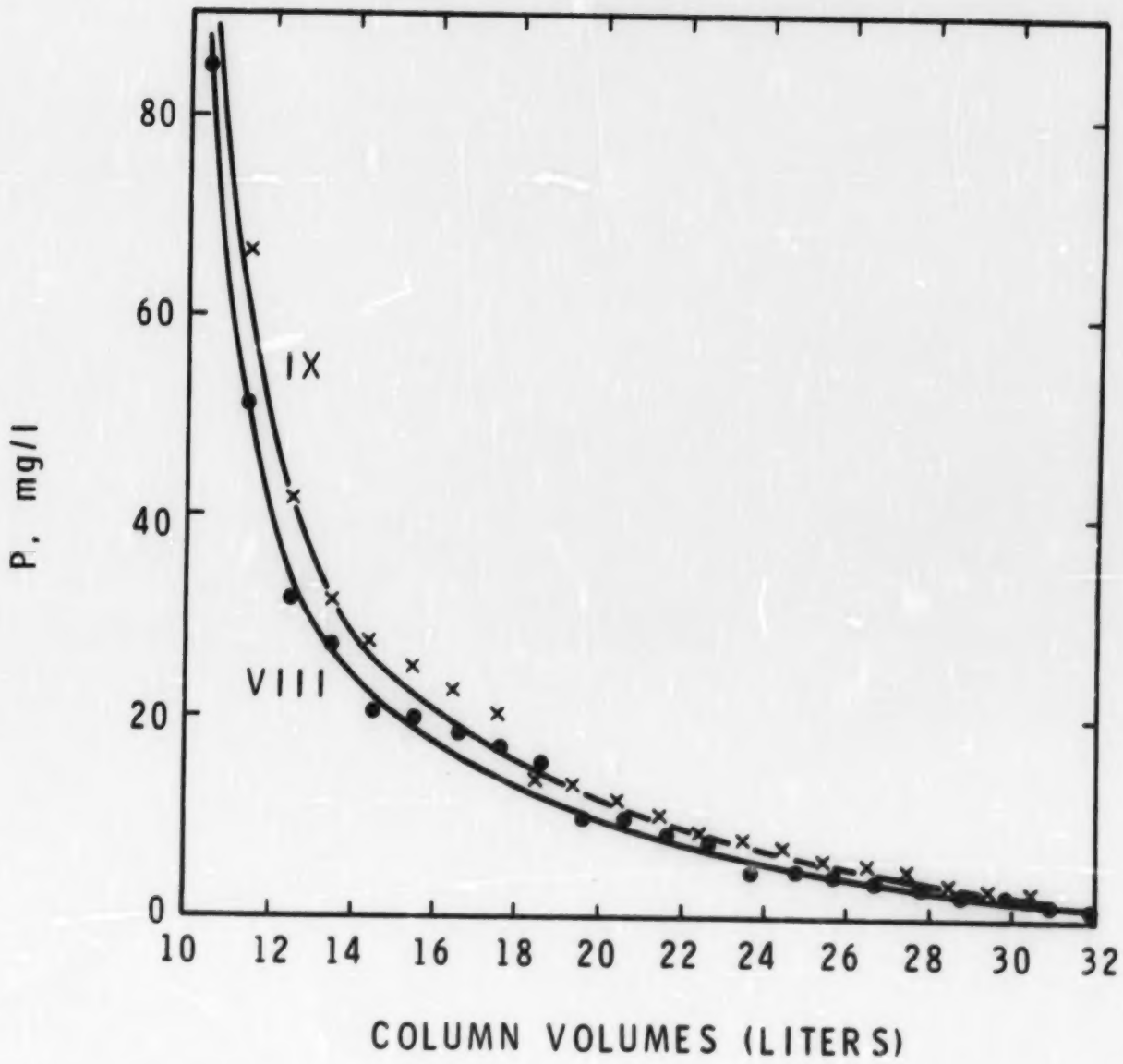


Figure 17. Phosphorus concentrations in the column washwater following elution of VIII and IX. Column, flow rate and temperature are the same as those given in Figure 16.

The charcoal column was 7.6 cm in diameter by 75 cm in height. The charcoal column was replaced on the ninth loading cycle by a 20 to 50 mesh sand filter 7.6 cm in diameter by 20 cm in height. The resulting phosphorus loading curve is given in Figure 14. The alumina and the influent solution were somewhat more colored than with the charcoal filtration, but the loading cycle was otherwise normal. Carbon treatment is probably not justifiable if phosphorus removal is the only goal.

The elution data of cycle IX are compared to that of cycle VIII in Figures 16 and 17. There was little difference between the sand and charcoal filtered elution data.

The NaOH solutions, after use, contained the color units shown in Table 5. The colors matched fairly well when determined by the standard platinum-cobalt method.

Table 5

Color test results on 2M NaOH elution following loading Cycle VIII

Cumulative Column Volumes	Color Units
2	5
3	125
4	175
5	45
6	35
7	25
8	15
9	5

Stirring the used NaOH with 10 to 20 g of $Ca(OH)_2$ resulted in removal of all color and phosphorus (and also CO_3^{-2}) from the solution. The resulting solids settled well and the Na H could be reused.

The preliminary laboratory work with phosphorus removal by adsorption on alumina columns, and subsequent treatment and reuse of eluting solutions, has shown that the process is technically feasible. Process scaleup to obtain engineering performance data is suggested as a means of substantiating economic feasibility.

CONCLUSIONS AND RECOMMENDATIONS

The removal of phosphorus from secondary sewage treatment effluent was successfully demonstrated with one liter alumina columns on a laboratory scale.

Ninety-five to plus 99% of the phosphorus was removed from a synthetic secondary sewage effluent by alumina beds producing an effluent that was 0.03 mg P/l, or less, at column flow rates of less than 10 column volumes/hr. The same phosphorus removal results were obtained with up to 500 column volumes of Richland trickling filter effluent. Regeneration of the alumina column was accomplished with 8 column volumes of 2 M NaOH. This regenerant solution was restored by the addition of a small amount of lime, removing the phosphorus as hydroxyapatite and carbonate as calcite. Thus, only a small volume, solid waste is produced by the process. Alumina losses of about 0.1% per elution cycle were indicated.

It is recommended that this promising phosphorus removal process be scaled up to a portable pilot plant size. More operating data is required at sites that can furnish different composition influents because treatment costs and phosphorus removal efficiencies probably will vary from site to site. The process should be demonstrated at several sites, in any case, for the benefit of interested personnel in the field. Some points that should be determined more precisely because of their effects on process costs include:

1) Measurement of alumina attrition and dissolution losses over several loading and eluting cycles,
2) More precise measurement of the quantity of lime that is necessary to render the spent regenerant solution reuseable,
3) Measure solid waste product volume per elution cycle,
4) Measure effect of column flow rate on phosphorus leakage, and
5) Measure effect of type of sewage treatment on subsequent phosphorus removal.

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SELECTED WATER RESOURCES ABSTRACTS
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10 Author(s): Ames, L. L.

16 Project Designation: FWPCA Program 17010, Contract No. 14-12-413. ~~FWQA~~

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25 Identifiers (Starred First): Phosphate removal, Alumina,

27 Abstract: A synthetic secondary sewage effluent containing 10 to 30 mg/liter phosphate, 300 mg/liter bicarbonate, 112 mg/liter Cl and 50 mg/liter sulfate as anions and 130 mg/liter Na, 60 mg/liter Ca, 25 mg/liter each of K and Mg and 20 mg/liter ammonium as cations was used with 7.6 ml alumina columns to study the effects of various compositional changes on phosphorus removal. The phosphorus capacity was about half for the solution containing no Ca or Mg as compared to solutions containing them. Probably adsorption onto the alumina occurs partly as a calcium or magnesium phosphorus complex rather than as a simple phosphorus anion. Increasing the competing sulfate concentration in the influent solution to 4800 mg/liter showed little effect on phosphorus adsorption. Raising the pH of the synthetic sewage effluent to greater than 8.0 led to precipitation of calcium carbonate on the alumina grains which progressively lowered alumina phosphorus capacity. This problem was not encountered when using actual sewage effluent. It was found that alumina columns could be satisfactorily regenerated with NaOH. (Knapp-USGS) (WRSIC abstract)

Abstractor: George Knapp 12-15-69 | Institution: U. S. Geological Survey, Water Resources Div.

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